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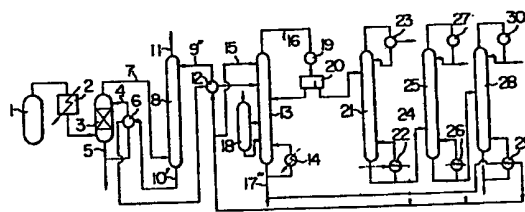
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### 54 Process for producing unsaturated nitrile.

57 A process for producing an unsaturated nitrile comprising the steps of water-cooling, in a quenching column, a reaction mixture containing the unsaturated nitrile, a saturated nitrile and prussic acid, said reaction mixture being obtained by ammoxidation of an olefin, absorbing the reaction mixture with the absorption water in an absorption column, subjecting the resulting absorption solution to extractive distillation in a stripping column by using solvent water, taking out a distillate containing the crude unsaturated nitrile and prussic acid from the top of the stripping column, and then removing the prussic acid, water and the like from the distillate by distillation in distillation columns of a de-prussic acid column, a dehydration column and a product column to obtain the unsaturated nitrile, wherein the solvent water obtained from the lower part of the stripping column and being substantially free from the unsaturated nitrile and prussic acid contained in the feed to the stripping column is recycled as the absorption water in the absorption column or the solvent water effluent from the acetonitrile-stripping column obtained by feeding the solvent water withdrawn from the lower part of the said stripping column to remove acetonitrile substantially is recycled as the solvent water in the stripping column and/or the absorption water in the absorption column, characterized in that when the absorption solution effluent from the stripping column is preheated with the solvent water withdrawn

from the lower part of the stripping column and/or the solvent water withdrawn from the lower part of the acetonitrile-stripping column and then fed to the stripping column, the absorption solution is preheated by previously passing the same through at least one column selected from the group consisting of the cooler for the circulating water in the quenching column, the condenser for the overhead vapor in the stripping column, the condenser for the overhead vapor in the dehydration column, and the condenser for the overhead vapor in the product column, and the solvent water is used, prior to pre-heating the above absorption solution, as a heat source of at least one column selected from the distillation columns in the de-prussic acid column, the dehydration column and the product column.



PROCESS FOR PRODUCING UNSATURATED NITRILE

1           This invention relates to a process for producing an unsaturated nitrile by ammoxidation of an olefin, for example, a process for producing acrylonitrile or methacrylonitrile by ammoxidation of propylene or  
5 isobutylene.

          The object of this invention is to provide a production process having a very high energy efficiency in which sensible or latent heat at a relatively low temperature generated in the production system which  
10 heat has never been able to be utilized is converted to a cooling or heating heat-source and effectively utilized.

          In the process for the production of an unsaturated nitrile by ammoxidation of an olefin, the reaction products at a high temperature are cooled with  
15 water and then absorbed in a large amount of water (for example, according to Japanese Patent Publication No. 657/66, absorption water is used in an amount of 17.8 times the weight of acrylonitrile), after which the  
20 resulting absorption solution is repeatedly subjected to distillation by heating and condensation by cooling, whereby the unsaturated nitrile is separated and purified from the by-products and the unreacted materials. Therefore, the energy required for heating  
25 and cooling has heretofore been very much and the pro-

1 portion of energy expense in the cost has been high.

The conventional process and the present process are concretely explained below referring to the accompanying drawings, in which Figs. 1 and 2 are flow sheets showing the conventional processes for producing acrylonitrile and Figs. 3, 4, 5 and 6 flow sheets showing the processes of this invention which appear hereinafter. In the drawings, 1 ... a reactor, 2 ... a heat exchanger, 3 ... a quenching column, 4 ... a line, 5 ... a line, 6 ... a cooler, 7 ... a line, 8 ... an absorption column, 9 ... a line, 9' ... a line, 9" ... a line, 10 ... a line, 10' ... a line, 10" ... a line, 11 ... a line, 12 ... a heat exchanger, 13 ... a recovery column, 14 ... a reboiler, 15 ... a line, 15' ... a line, 15" ... a line, 16 ... a line, 17 ... a line, 17' ... a line, 17" ... a line, 18 ... an acetonitrile-stripping column, 19 ... a condenser, 20 ... a decanter, 21 ... a de-prussic acid column, 22 ... a reboiler, 23 ... a condenser, 24 ... a line, 25 ... a dehydration column, 26 ... a reboiler, 27 ... a condenser, 28 ... a product column, 29 ... a reboiler, and 30 ... a condenser.

In Fig. 1, in a reactor 1, continuously fed propylene, ammonia and air undergo ammoxidation in the gas phase at a high temperature in the presence of an oxidation catalyst to give a mixture of unreacted compounds and reaction products such as acrylonitrile, acetonitrile, prussic acid and high boiling organic matters. This gaseous mixture at a high temperature is sent via a heat

1 exchanger 2 to a quenching column 3, and brought into  
contact with circulating water for cooling which is  
flowing down via a line 4 from the top of the column to  
be cooled to a low temperature. In this cooling  
5 step, the high boiling organic matters and the water  
generated are incorporated into the circulating water to  
be removed, and if necessary, a mineral acid is added to  
the circulating water to remove the unreacted ammonia in  
the reaction product gas. The heated circulating water  
10 is withdrawn from the bottom of the column through a  
line 5, cooled in a cooler 6, and then circulated and  
fed through a line 4 to the top of the column again, and  
a part of it is then eliminated from the system.

The gas introduced from the top of the  
15 quenching column 3 through a line 7 to the lower part of  
an absorption column 8 is contacted with the absorption  
water fed via a line 9 which flows down in the column  
from the top thereof, and the acrylonitrile, aceto-  
nitrile and prussic acid are absorbed into the absorp-  
20 tion water. The resulting absorption solution is taken  
out as a bottom stream through a line 10, and the unab-  
sorbed gas is discharged from the top of the column  
through a line 11.

The absorption solution is passed through a  
25 heat exchanger 12, heated therein, fed to a recovery  
column 13 from a somewhat upper part thereof, and then  
heated by means of a reboiler 14. The recovery column  
usually has at least 50, preferably 60 to 100 trays, and

1 the absorption solution is countercurrently contacted  
with the solvent water sent via a line 15 to the top of  
the column to undergo extractive distillation. Crude  
acrylonitrile vapor containing prussic acid and water is  
5 distilled out from the top of the column via a line 16,  
while the solvent water is taken out from the bottom of  
the column via a line 17. Most of the acetonitrile in  
the absorption solution is separated by distillation in  
an acetonitrile-stripping column 18 attached to the  
10 recovery column 13. The solvent water substantially  
free from the acetonitrile which has been taken out  
through the line 17 is sent via the line 15 to the  
recovery column 13, while a part thereof is passed  
through the heat exchanger 12 to be cooled and then fed  
15 as absorption water via the line 9 to the absorption  
column 8. The crude acrylonitrile vapor distilled out  
through the line 16 is cooled in a condenser 19, and the  
condensate is separated into an oily layer and an  
aqueous layer in a decanter 20. The oily layer is sent  
20 to a de-prussic acid column 21, and the aqueous layer is  
returned to the recovery column 13.

The de-prussic acid column 21 is heated by  
means of a reboiler 22, and prussic acid is taken out by  
distillation from the top of the column and then sub-  
25 jected to fractional condensation in a condenser 23,  
whereby prussic acid vapor is separated. The bottom  
stream is sent through a line 24 to a dehydration column

1 25. The dehydration column 25 is heated by means of a  
reboiler 26, and the vapor taken out by distillation  
from the top of the column is condensed in a condenser  
27, and separated into an oily layer and an aqueous  
5 layer, after which the oily layer is dehydrated. The  
bottom stream is sent to a product column 28. The product  
column 28 is heated by means of a reboiler 29, and the  
vapor taken out by distillation from the top of the  
column is condensed in a condenser 30 to obtain acrylo-  
10 nitrile having the desired quality, while the bottom  
stream is discharged.

The conventional process for producing acrylo-  
nitrile is as described above, and involves many heating  
steps and cooling steps. That is to say, the recovery  
15 column 13, the de-prussic acid column 21, the dehydra-  
tion column 25 and the product column 28 are equipped  
with the reboilers 14, 22, 26 and 29, respectively, and  
the condensers 19, 23, 27 and 30, respectively, and the  
quenching column 3 is equipped with the cooler 6. In  
20 order to increase the energy efficiency of the process  
in which heating and cooling are repeated, various coun-  
termeasures have heretofore been taken. For example,  
according to Japanese Patent Application Kokai  
(Laid-Open) No. 81,848/80, it has been proposed that  
25 solvent water at a high temperature ( $110^{\circ}$  to  $130^{\circ}\text{C}$ )  
taken out of the recovery column is used as a reboiler  
heat source for the de-prussic acid column and the pro-

1 duct column, after which the absorption solution is pre-  
heated in the heat exchanger 12 and used as the absorp-  
tion water. However, this method has been disadvan-  
tageous in that since the solvent water becomes cooled,  
5 the quantity of heat becomes insufficient for preheating  
(in the heat exchanger 12 in Fig. 1) the absorption  
water to be fed to the recovery column 13, so that an  
extra heat source for the recovery column (the reboiler  
14) is needed, or in that the heat-conductive area of  
10 the heat exchanger 12 has to be made extremely large.

In Fig. 2, the same procedure as in Fig. 1 is  
repeated, except that a part of the solvent water is  
withdrawn through a line 15' without being passed  
through the acetonitrile-stripping column and is passed  
15 through the heat-exchanger 12 to lower the temperature  
of the solvent water, and then is fed to the absorption  
column 8 as the absorption water through a line 9',  
while the solvent water is withdrawn from the bottom  
through a line 17' and sent to the recovery column 13.

20 This invention has been made in view of the situa-  
tion described above, and the gist thereof is a process for  
producing an unsaturated nitrile comprising the steps of  
water-cooling, in a quenching column, a reaction mixture  
containing the unsaturated nitrile, a saturated nitrile  
25 and prussic acid which mixture is obtained by ammoxida-  
tion of an olefin, absorbing the reaction mixture with  
absorption water in an absorption column, subjecting the

1 resulting absorption solution to extractive distillation  
in a recovery column by using solvent water, taking out  
a distillate containing the crude unsaturated nitrile  
and prussic acid from the top of the recovery column,  
5 and then separating prussic acid, water and the like  
from the distillate by distillation in distillation  
columns such as a de-prussic acid column, a dehydration  
column and a product column to obtain the unsaturated  
nitrile, and recycling, as the absorption water in the  
10 absorption column and as the solvent water in the  
recovery column, the solvent water obtained from the  
lower part of the recovery column, free from aceto-  
nitrile, which process is characterized in that when the  
absorption solution effluent from the absorption column  
15 is preheated with the solvent water free from aceto-  
nitrile and then fed to the recovery column, said  
absorption water is preheated by previously passing it  
through at least one member selected from the group con-  
sisting of the cooler for the circulating water in the  
20 quenching column and the condensers for overhead vapors  
of the dehydration column, the product column and the  
recovery column, while said solvent water is used as a  
heat source for at least one column selected from the  
group consisting of distillation columns such as de-  
25 prussic acid column, dehydration column and product  
column before preheating said absorption water. That is  
to say, this invention is characterized in that the

1 absorption water taken out of the absorption column is  
preheated by passing it through (i) the cooler for the  
circulating water in the quenching column, (ii) the con-  
denser for overhead vapor of the recovery column, (iii)  
5 the condenser for overhead vapor of the dehydration  
column, and (vi) the condenser for overhead vapor of the  
product column, and in that the solvent water effluent  
from the bottom of the recovery column is used as a  
heat source for at least one column selected from the  
10 group consisting of (i) the de-prussic acid column, (ii)  
the dehydration column, and (iii) the product column,  
and then heat-exchanged with the aforesaid preheated  
absorption water. Therefore, the solvent water from the  
bottom of the recovery column is not only utilized as a  
15 heat source for at least one member selected from the  
group consisting of the de-prussic acid column, the  
dehydration column, and the product column, but also  
heat-exchanged with the preheated absorption water,  
whereby the absorption solution can be preheated to the  
20 desired temperature. Accordingly, no extra heat source  
for distillation in the recovery column is needed and  
that it is not necessary to improve the capacity of the  
heat-exchanger to preheat the absorption solution.

On the other hand, the absorption solution  
25 effluent from the absorption column at a low temperature  
is passed through at least one column selected from the  
group consisting of the cooler for the circulating water

1 in the quenching column and the condensers of the  
distillation columns, and utilized for cooling the cir-  
culating water and for condensing the overhead vapor,  
and hence regeneration energy for the cooling water used  
5 can be saved.

That is to say, it has been found that when  
the absorption water from the absorption column is  
passed through at least one column selected from the  
group consisting of the above-mentioned cooler and con-  
10 densers, there can be obtained a stable process by which  
the solvent water from the bottom of the recovery column  
can be utilized as a heat source for at least one column  
selected from the group consisting of the de-prussic  
acid column, the dehydration column and the product  
15 column, so that the heat energy can very effectively be  
saved.

The quality of the product in the steps in the  
present process is not affected at all.

A preferable process of this invention is  
20 explained below referring to the drawings.

As shown in Fig. 3, the absorption solution at  
15° to 35°C effluent from the absorption column 8 is  
passed through the cooler 6 for the circulating water in  
the quenching column 3 and heated to 35° to 50°C with  
25 the circulating water heated to 30° to 60°C before being  
preheated with the solvent water in the heat exchanger  
12. On the other hand, the solvent water at 100° to

1 120°C effluent from the bottom of the recovery column  
13 is used as a heat source for the reboiler 29 of the  
product column 28, and then passed through the heat  
exchanger 12 for preheating the absorption solution, to  
5 preheat the absorption solution to 70° to 90°C, which is  
then fed to the recovery column 13.

As a result, the heat sources can be reduced  
by utilizing the solvent water effluent from the reco-  
very column as a heat source for the product column 28.  
10 At the same time, the absorption solution can be pre-  
heated to such a suitable temperature as before without  
any substantial increase of the capacity of the heat  
exchanger 12, so that no extra heat source for the  
recovery column is needed.

15 The cooling water for the cooler 6 in the  
quenching column 3 can be saved as much as the quantity  
of heat recovered as described above.

In this process, as described above, the  
solvent water effluent from the recovery column 13 is  
20 used as a heat source for the reboiler 29 of the product  
column 28, though it may be further used also as a heat  
source for one or more distillation columns such as the  
de-prussic acid column 21 and the dehydration column 25.

As shown in Fig. 4, the absorption solution at  
25 15° to 35°C effluent from the absorption column 8 is  
passed through the condenser 19 of the recovery column  
13 and heated to 35° to 50°C with the sensible heat and

1 latent heat of overhead vapor at  $70^{\circ}$  to  $90^{\circ}\text{C}$  in the  
recovery column before being preheated with the solvent  
water in the heat exchanger 12. On the other hand, the  
solvent water at  $100^{\circ}$  to  $130^{\circ}\text{C}$  effluent from the bottom  
5 of the recovery column 13 is used as a heat source for  
the reboiler 29 of the product column 28, and then  
passed through the heat exchanger 12 for preheating the  
absorption solution, to preheat the absorption solution  
to  $70^{\circ}$  to  $90^{\circ}\text{C}$ , which is then fed to the recovery  
10 column 13.

As a result, the heat sources can be reduced  
by utilizing the solvent water effluent from the  
recovery column as a heat source for the product column  
28. At the same time, the utilization of the sensible  
15 heat and latent heat of the overhead vapor in the top of  
the recovery column 13 makes it possible to preheat the  
absorption solution to such a suitable temperature as  
before without any substantial increase of the capacity  
of the heat exchanger 12, so that no extra heat source  
20 for the recovery column is needed. Moreover, the  
cooling water for the condenser 19 becomes unnecessary.  
In this process, as described above, the solvent water  
effluent from the recovery column 13 is used as a heat  
source for the reboiler 29 of the product column 28,  
25 though it may be further used also as a heat source for  
one or more distillation columns such as the de-prussic  
acid column 21 and the dehydration column 25. Although

1 as described above, the absorption solution from the  
absorption column is preheated with the overhead vapor  
in the recovery column, the same effect can be obtained  
by preheating it with overhead vapor in the dehydration  
5 column 25 or the product column 28. It may be preheated  
stepwise with two or more kinds of overhead vapors.

As shown in Fig. 5, the absorption solution  
effluent from the absorption column 8 is, prior to being  
preheated with the solvent water in the heat-exchanger  
10 12, passed through the cooler 6 for the circulating  
water in the quenching column 3 to elevate the tem-  
perature of the absorption water with the circulating  
water having an elevated temperature. On the other  
hand, the high temperature solvent water substantially  
15 freed from the unsaturated nitrile and prussic acid con-  
tained in the feed to the recovery column withdrawn from  
the side of the recovery column 13 through the line 15"  
without passing through the acetonitrile-stripping  
column is used as a heat source for the reboiler 29 in  
20 the product column 28, and thereafter passed through the  
heat exchanger for preheating the absorption solution to  
preheat the absorption solution, after which the absorp-  
tion solution thus preheated is fed to the recovery  
column 13.

25 As a result, the solvent water effluent from  
the recovery column can be utilized as the heat source  
in the product column 28 to save the heat source. At

1 the same time, the absorption solution can be preheated  
to an optimum temperature without substantially  
increasing the capacity of the heat-exchanger 12, so  
that no extra heat source for the recovery column is  
5 needed. Moreover, the cooling water for the cooler 6 in  
the quenching column 3 is remarkably saved.

In this example, the solvent water effluent  
from the recovery column 13 is used as the heat source  
of the reboiler 29 in the product column. However, it  
10 may also be used as a heat source of at least one of the  
distillation columns of the de-prussic acid column 21,  
the dehydration column 25 and the like.

As shown in Fig. 6, the absorption solution  
effluent from the absorption column 8 is, prior to being  
15 preheated with the solvent water in the heat exchanger  
12, passed through the condenser 19 in the recovery  
column 13 to elevate the temperature thereof with the  
sensible or latent heat of the overhead vapor of the  
recovery column. On the other hand, the high tem-  
20 perature solvent water withdrawn from the side part of  
the recovery column without passing through the  
acetonitrile-stripping column and substantially freed  
from the fraction comprising the unsaturated nitrile and  
prussic acid contained in the feed to the recovery  
25 column is used as the heat source of the reboiler 29 in  
the product column 28, and thereafter passed through the  
heat exchanger 12 for preheating the absorption solution

1 to preheat the absorption solution, after which the  
absorption solution is sent to the recovery column 13.

As a result thereof, the solvent water  
effluent from the recovery column is utilized as the  
5 heat source of the product column 28, whereby the saving  
of heat source is made possible, and at the same time,  
the absorption solution can be preheated to an optimum  
temperature without increasing the capacity of the heat  
exchanger 12, so that no extra heat source for the reco-  
10 very column is needed. In addition, the cooling water  
for the condenser 19 in the recovery column is made  
unnecessary.

In this example, the solvent water is used as  
the heat source of the product column 28 and may also be  
15 used as a heat source of at least one of the distilla-  
tion columns of the de-prussic acid column, the dehydra-  
tion column 25 and the like. Moreover, in this example,  
the absorption solution is preheated with the overhead  
vapor of the recovery column, but may also be preheated  
20 with the overhead vapor of the dehydrated column 25 or  
the product column 28 to obtain a similar effect.  
Furthermore, it may be preheated at multiple stages with  
at least two overhead vapors.

This invention is as described above, and  
25 enables the reduction of the heat sources for the  
distillation columns such as the de-prussic acid column,  
the dehydration column and the product column and the

- 1 saving of the heat source for the recovery column, and  
hence requires substantially no increase of the capacity  
of the heat exchanger for preheating the absorption  
solution. Furthermore, the cooling water for the cir-  
5 culating water in the quenching column and the cooling  
water for condensation in distillation columns such as  
the recovery column, the dehydration column and the  
product column can be saved, and therefore, the energy  
efficiency can greatly be improved.

WHAT IS CLAIMED IS

1. A process for producing an unsaturated nitrile comprising the steps of water-cooling, in a quenching column, a reaction mixture containing the unsaturated nitrile, a saturated nitrile and prussic acid which mixture is obtained by ammoxidation of an olefin, absorbing the reaction mixture with the absorption water in an absorption column, subjecting the resulting absorption solution to extractive distillation in a recovery column by using solvent water, taking out a distillate containing the unsaturated nitrile and prussic acid from the top of the recovery column, and then separating prussic acid, water and the like from the distillate by distillation in distillation columns of a de-prussic acid column, a dehydration column and a product column to obtain the unsaturated nitrile, wherein the solvent water obtained from the side part of the recovery column substantially free from the unsaturated nitrile and prussic acid contained in the feed to the recovery column is recycled as the absorption water in the absorption column, or the solvent water withdrawn from the lower part of the said recovery column is fed to the acetonitrile-stripping column to remove substantially all the acetonitrile, and the thus obtained solvent water is recycled as the solvent water in the recovery column and/or as the absorption water in the absorption column, characterized in that when the absorption solu-

tion effluent from the absorption column is preheated with the aforesaid solvent water withdrawn from the lower part of the recovery column and/or the solvent water withdrawn from the side part of the recovery column without passing through the acetonitrile stripping column, and then fed to the recovery column, said absorption solution is preheated by previously passing it through at least one column selected from the group consisting of the cooler for the circulating water in the quenching column, the condenser for the overhead vapor in the recovery column, the condenser for the overhead vapor in the dehydration column and the condenser for the overhead vapor in the product column, and the above-mentioned solvent water is used as a heat source for at least one column selected from the group consisting of distillation columns of the de-prussic acid column, the dehydration column, and the product column before preheating said absorption solution with the solvent water.

FIG. 1

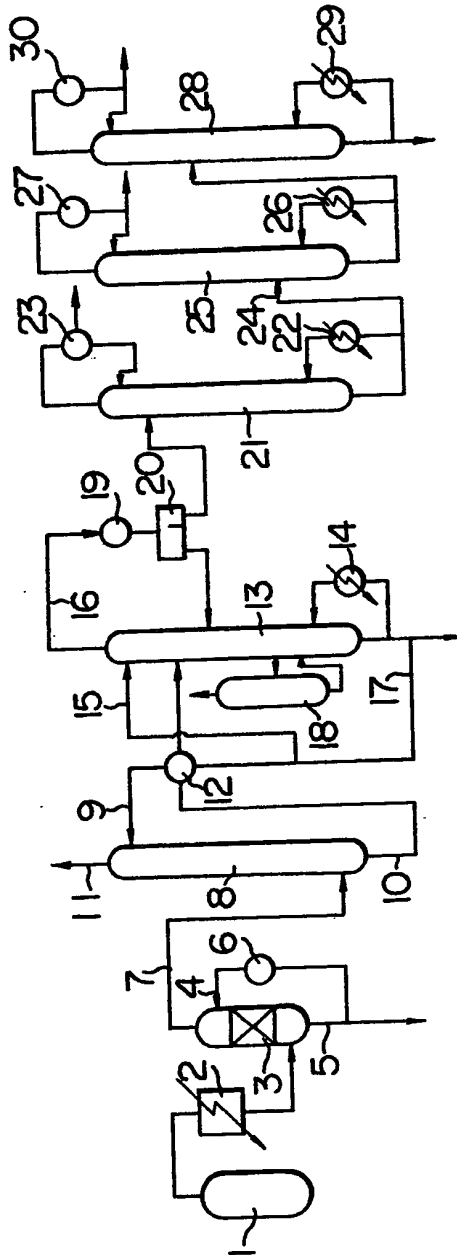


FIG. 2

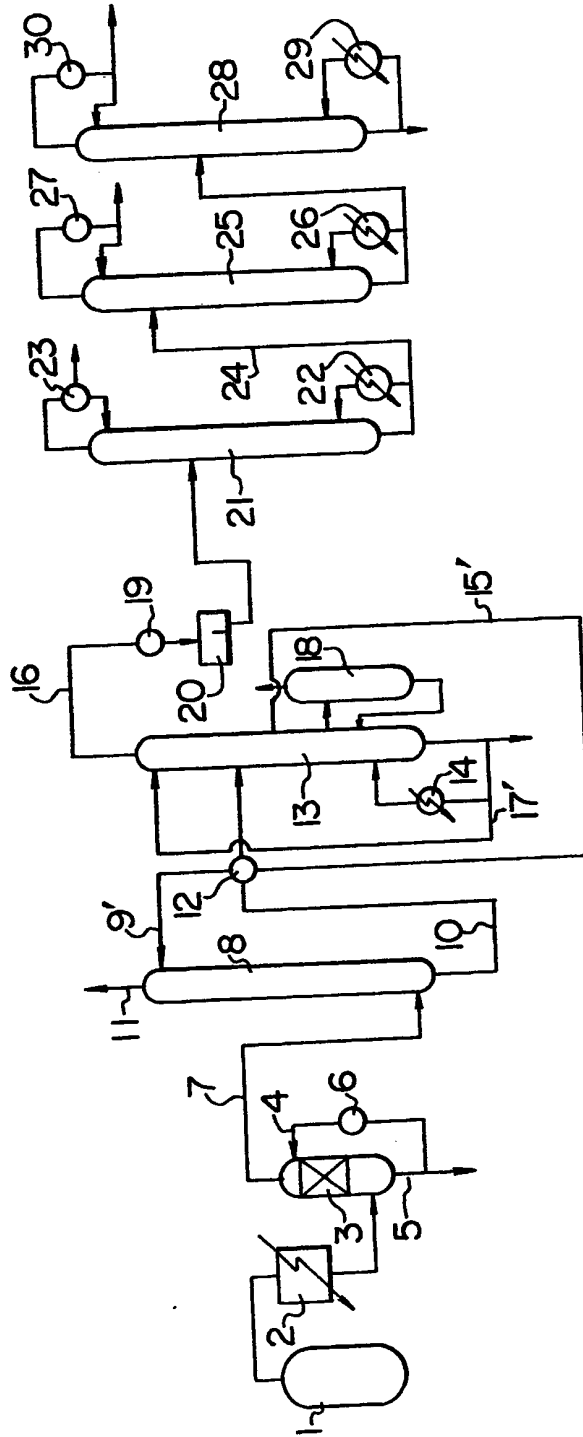


FIG. 3

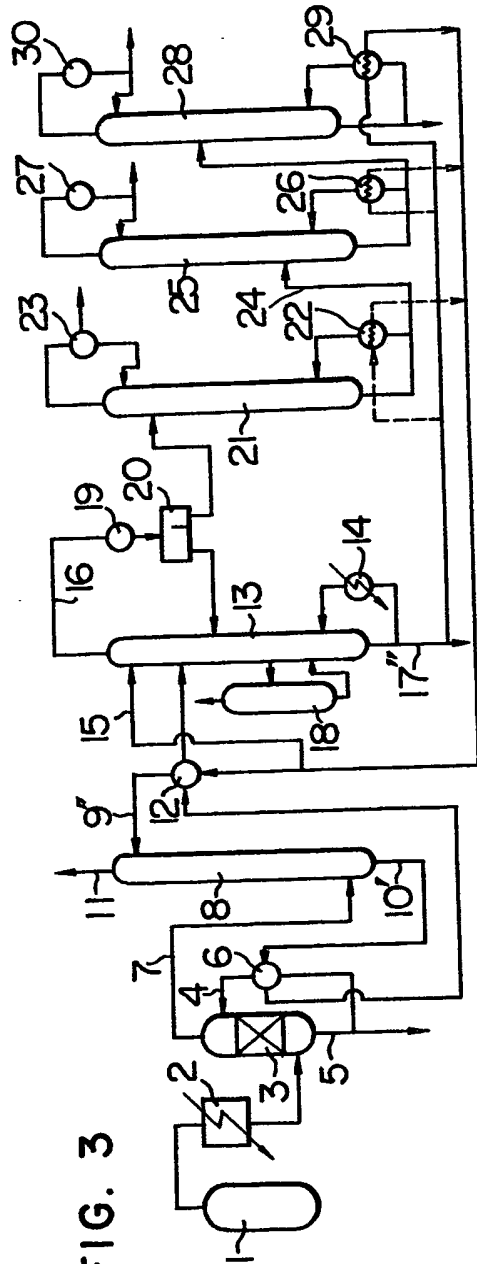


FIG. 4

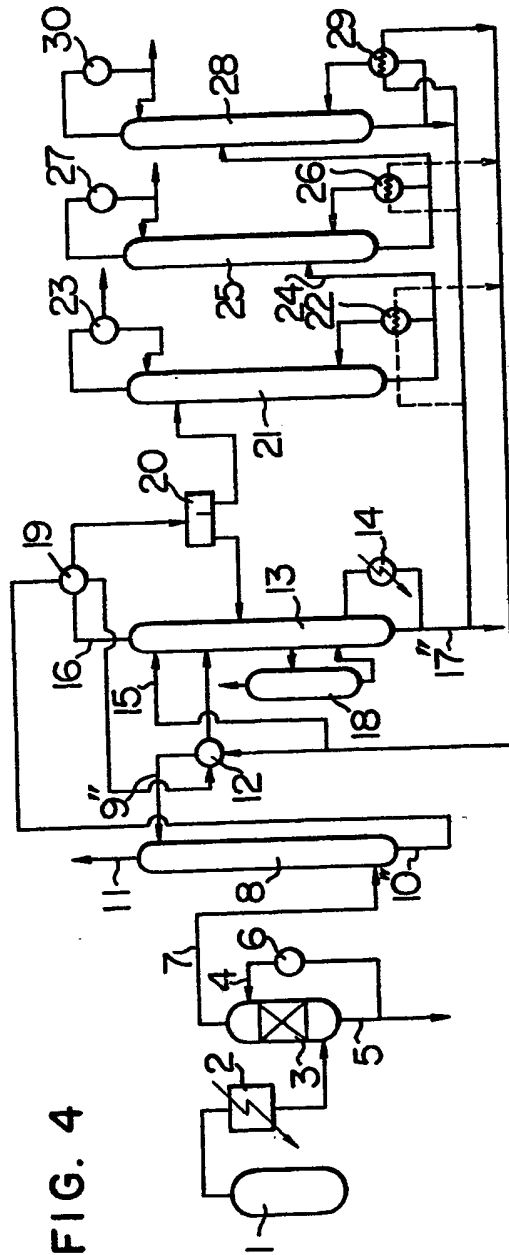
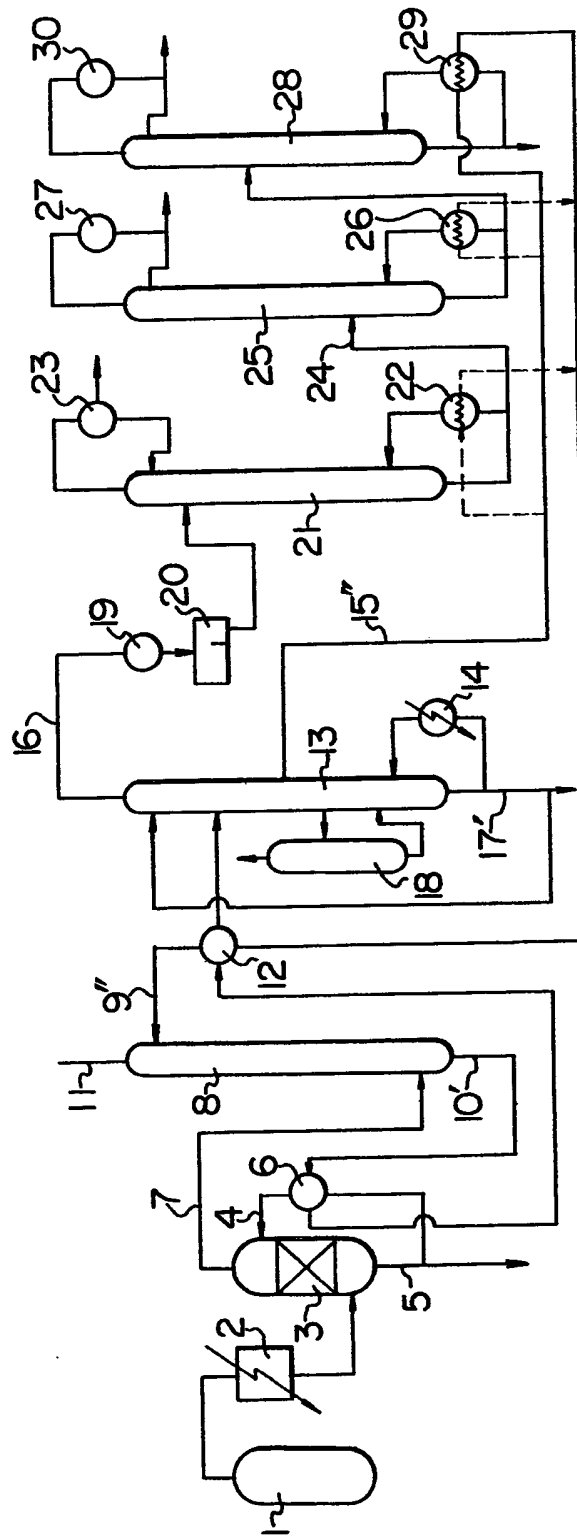


FIG. 5







European Patent  
Office

# EUROPEAN SEARCH REPORT

0053518  
Application number

EP 81 30 5681.9

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>EP - A2 - 0 012 039</u> (STANDARD OIL CO.) * claims 1 to 7; page 2, lines 13 to 19; page 3, paragraph c; fig. *	1	C 07 C 120/14 C 07 C 121/32
A	<u>US - A - 3 895 050</u> (BADGER CO.) * column 5, line 24; column 6, lines 12 to 15 *		TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
A	<u>DE - A - 1 593 357</u> (SOCIETA EDISON) * page 9, line 1; example 1 *		C 07 C 120/14 C 07 C 121/32
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons
			&: member of the same patent family, corresponding document
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			
Place of search Berlin		Date of completion of the search 24-02-1982	Examiner BREW